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Attorney's Docket No. 1999DE122

☐ Duplicate
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

NEW UTILITY PATENT APPLICATION TRANSMITTAL

Sir:

Transmitted for filing on May 25, 2000 is the patent application of

Inventors: **Norbert WEFERLING**
Martin SICKEN

For: **PROCESS FOR PREPARING (METAL) ALKYLPHOSPHONITES I**

1. This new application is for a(n)
☒ Original (nonprovisional)
☐ Divisional
☐ Continuation
☐ Continuation-in-Part
2. Papers enclosed that are required for filing date under 37 CFR 1.53(b) (Regular)
14 Pages of Specification and Claims (19 in number)
1 Pages of Abstract
0 N/A sheets of drawings
3. Additional papers enclosed:
☒ Preliminary Amendment
☐ Information Disclosure Statement
☐ Form PTO-1449
☐ References Cited
4. Declaration or Oath:
☒ Enclosed - EXECUTED BY INVENTORS
☐ Not Enclosed

5. An assignment of the invention to Clariant GmbH is attached. A separate "Assignment Recordation Form Cover Sheet" is also attached.
6. Certified copy of application from which priority is claimed will follow.

Country	Application No.	Filed
Federal Republic of Germany	199 23 830.8	May 25, 1999

7. Fee calculation

<u>CLAIMS AS FILED</u>				
Basic Filing Fee				\$690.00
<u>Number Filed</u>	<u>Number Extr</u>		<u>Rate</u>	
	<u>a</u>			
Total Claims: 19	Minus 20	=8	X \$18.00	
Independent Claims: 1	Minus 3	=	X \$78.00	
Multiple Dependent Claims (if any)			+\$260.00	
TOTAL FEE DUE				\$690.00

- ☐ Amendment canceling extra claims is enclosed.
- ☒ Amendment deleting multiple-dependencies is enclosed.
- ☐ Fee for extra claims is not being paid at this time.

Filing Fee Calculation \$690.00

8. Fee Payment Being Made at this Time

- ☐ Not enclosed -- No filing fee is to be paid at this time.
- ☒ Enclosed
- ☒ Basic Filing Fee \$690.00
- ☒ Assignment Recordation Fee 40.00

Total Fees Enclosed \$730.00

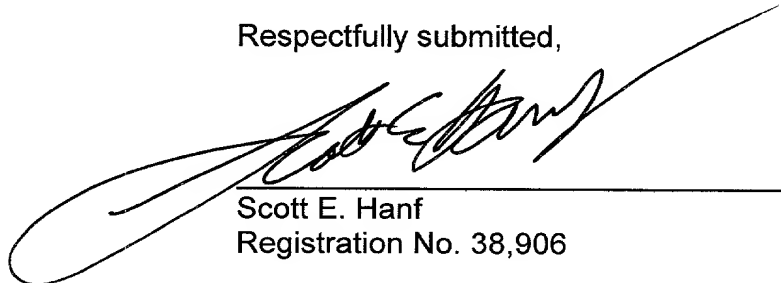
9. Method of Payment

- ☒ The total filing fee calculated above is authorized to be charged to Deposit Account No. 03-2060 for which purpose a duplicate copy of this cover sheet is attached.

10. Authorization to charge additional fees/instructions as to overpayment

- X The Commissioner is also authorized to credit any overpayments or charge any additional fees required under 37 CFR 1.16 (application filing fees) or 37 CFR 1.17 (application processing fees) during the prosecution of this application, including any related application claiming benefit hereof pursuant to 35 USC §120 (e.g., continuations, divisionals and/or CIPs under 37 CFR §1.53(b) and/or continuations, divisionals and/or CIPs under 37 CFR §1.53(b)) to maintain pendency hereof of any such related application.

Respectfully submitted,



Scott E. Hanf
Registration No. 38,906

Clariant Corporation
Industrial Property Department
4331 Chesapeake Drive
Charlotte, North Carolina 28216
Telephone: 704/395-6712
Facsimile: 704/395-6727

CERTIFICATION UNDER 37 CFR 1.10

Express Mail Mailing Label Number: EJ913191586US
Date of Mailing: May 25, 2000

I hereby certify that on the date indicated above, this new U.S. patent application and the papers indicated as enclosed therein, is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee" addressed to: Assistant Commissioner for Patents, Box Patent Application, Washington, D.C. 20231, in accordance with 37 CFR 1.10.



Signature of Person Mailing the Application

Vicki L. Sgro
Typed Name of Person Mailing the Application

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re U.S. patent of :
Norbert WEFERLING, et al. :
Serial No. to be assigned :
Filed: May 25, 2000 :
For: PROCESS FOR PREPARING :
(METAL) ALKYLPHOSPHONITES I :
:

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
And Trademarks
Washington, DC 20231

Dear Sir:

Preliminary to the examination of the above-identified application, please enter the following preliminary amendment.

IN THE SPECIFICATION:

Page 1, line 1, insert "PROCESS FOR PREPARING (METAL) ALKYLPHOSPHONITES I".

Page 1, line1, insert --BACKGROUND OF THE INVENTION--.

Page 3, line 12, insert --SUMMARY OF THE INVENTION--.

Page 4, line 1, insert --DESCRIPTION OF THE PREFERRED EMBODIMENTS--.

Page 10, line 1, insert --EXAMPLES--.

Page 11, line 1, delete "Patent claims" and substitute therefor --CLAIMS--.

Page 15, before line 1, delete "Process for the preparation of (metal) salts of alkylphosphonous acids I".

Page 15, line 1, delete "Abstract" and substitute therefor --ABSTRACT OF THE DISCLOSURE--.

IN THE CLAIMS:

Please amend the claims as follows:

Claim 3, line 1, delete "or 2".

Claim 4, lines 1 and 2, delete "one or more of claims 1 to 3," and substitute therefor, --claim 1, --.

In re U.S. patent of
Norbert WEFERLING, et al. :
Serial No. to be assigned :
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For: PROCESS FOR PREPARING :
(METAL) ALKYLPHOSPHONITES I :
Page 2

Claim 5, lines 1 and 2, delete "one or more of claims 1 to 4," and substitute therefor --claim 1,--.

Claim 6, lines 1 and 2, delete "one or more of claims 1 to 5," and substitute therefor --claim 1,--.

Claim 7, lines 1 and 2 , delete "one or more of claims 1 to 6," and substitute therefor --claim 1,--.

Claim 9, lines 1 and 2 , delete "one or more of claims 1 to 8," and substitute therefor --claim 1,--.

Claim 10, lines 1 and 2, delete "one or more of claims 1 to 9," and substitute therefor --claim 1,--.

Claim 11, lines 1 and 2, delete "one or more of claims 1 to 10," and substitute therefor --claim 1,--.

Claim 12, lines 1 and 2, delete "one or more of claims 1 to 11," and substitute therefor --claim 1,--.

Claim 13, lines 1 and 2, delete "one or more of claims 1 to 12," and substitute therefor --claim 1,--.

Claim 14, lines 1 and 2, delete "one or more of claims 1 to 13," and substitute therefor --claim 1,--.

Claim 15, lines 2 and 3, delete "one or more of claims 1 to 14," and substitute therefor --claim 1,--.

Claim 16, lines 1 and 2, delete "one or more of claims 1 to 14," and substitute therefor --claim 1,--.

Claim 17, lines 1 and 2, delete "one or more of claims 1 to 14," and substitute therefor --claim 1,--.

Claim 18, lines 1 and 2, delete "one or more of claims 1 to 14," and substitute therefor --claim 1,--.

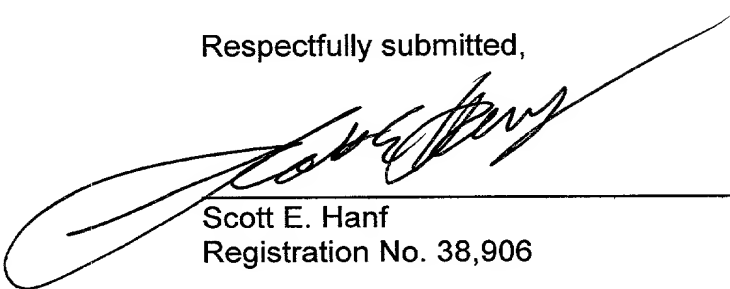
In re U.S. patent of
Norbert WEFERLING, et al. :
Serial No. to be assigned :
Filed: May 25, 2000 :
For: PROCESS FOR PREPARING :
(METAL) ALKYLPHOSPHONITES I :
Page 3

Claim 19, lines 2 and 3, delete "one or more of claims 1 to 14," and substitute therefor --claim 1,--.

REMARKS

Entry of the above amendment is respectfully requested.

Respectfully submitted,



Scott E. Hanf
Registration No. 38,906

Clariant Corporation
Industrial Property Department
4331 Chesapeake Drive
Charlotte, North Carolina 28216
Telephone: 704/395-6712
Facsimile: 704/395-6727

The invention relates to a process for the preparation of (metal) salts of alkylphosphonous acids, and to the use of the (metal) salts of alkylphosphonous acids prepared by this process.

5

Organic phosphorus compounds are increasing in industrial importance. They are employed principally for the preparation of herbicides or as herbicides themselves, as extractants and as flame retardants. The starting materials used are preferably PH_3 and phosphorus halides, which must themselves in turn be prepared from yellow phosphorus.

Hitherto, only a few processes were known with which organic phosphorus compounds having more than one phosphorus-carbon bond can be prepared from simple starting materials.

The reaction of red phosphorus in the superbasic medium dimethyl sulfoxide/potassium hydroxide (DMSO/KOH) with acetylenes or olefins as alkylating agent (Trofimov et al., Phosphorus, Sulfur and Silicon 55, 271, 1991) preferentially gives triorganylphosphines and triorganylphosphine oxides.

25

The alkylation of red phosphorus using acrylonitrile under the abovementioned conditions with ultrasound treatment of the reaction mixture gives predominantly secondary phosphine oxide. If 1,1-diphenylethylene is employed, tert-phosphine oxide (30%), sec-phosphine oxide (10%) and phosphinic acid (35%) are obtained [D. Semenzin et al., Tetrahedron Letters 35, 3297, 1994].

10 It has also been attempted (Trofimov et al., Main Group Chem. News 4, 18, 1996, Phosphorus, Sulfur and Silicon, 109/110, 601, 1996) to react elemental phosphorus in its red modification with alkyl halides in the presence of potassium hydroxide, water, dioxane and a phase-
15 transfer catalyst. The main product found comprised tert-phosphine oxides (up to 75% in the case of benzyl bromide, about 60 - 65% in the case of butyl bromide). As byproducts, sec-phosphine oxides and phosphinic acid esters are obtained with 19% and 6% respectively, but
20 the former only in the presence of zinc powder as reducing agent.

However, the abovementioned processes have the disadvantage that first of all the red phosphorus or
25 organophosphorus intermediates have to be prepared. The processes are technically very complex and consequently

also not economical, and the products obtained often have to be purified subsequently at great effort. In particular, the specific preparation of certain compounds in high yield is frequently particularly
5 difficult.

In addition, a number of starting materials, such as halogen-containing phosphorus compounds or phosphines, are unsuitable from the very beginning for a large-
10 scale and economical process owing to their environmental toxicity.

There is therefore a demand for a process for the preparation of (metal) salts of alkylphosphonous acids
15 which can be carried out in a simple manner and in which uniform products are obtained in high yield. A process of this type should also be clearly superior to those known hitherto in economic and environmental terms.

20

The invention therefore has the object of providing a process for the preparation of (metal) salts of alkylphosphonous acids which avoids the abovementioned disadvantages and with which the desired end products
25 can be prepared without difficulty.

This object is achieved by a process of the type described at the outset, which comprises reacting elemental yellow phosphorus with halogen-free alkylating agents in the presence of at least one base.

5

The reaction is preferably carried out in a two-phase system comprising at least one base and an organic solvent.

10 The alkylating agents are preferably dialkyl sulfates, trialkyl phosphates, dialkyl carbonates and/or formic acid ortho-esters. Particular preference is given to dimethyl sulfate.

15 The organic solvents employed are preferably straight-chain or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible or only partially water-miscible alcohols or ethers, alone or in combination with one another.

20

The organic solvent employed is particularly preferably toluene, alone or in combination with alcohols.

The bases are preferably hydroxides, carbonates,
25 bicarbonates, amides, alkoxides and/or amine bases.

Particular preference is given to the aqueous alkali metal hydroxides.

The reaction is preferably carried out in the presence
5 of a phase-transfer catalyst.

The phase-transfer catalyst is preferably a tetraalkylphosphonium halide, triphenylalkylphosphonium halide or tetraorganylammonium halide.

10

The temperature in the reaction is preferably from -20 to +60°C.

The temperature is particularly preferably from 0 to
15 30°C.

The reaction is preferably carried out under a pressure of from 0 to 10 bar.

20 The process according to the invention is preferably carried out by suspending or dissolving the yellow phosphorus in a solvent or solvent mixture and then reacting it with a halogen-free alkylating agent and at least one base.

25

The yellow phosphorus and the halogen-free alkylating agent are preferably reacted with one another in a molar ratio of from 1:1 to 1:3, where the molar ratio of yellow phosphorus to base is from 1:1 to 1:5.

5

The two-phase system obtained after the reaction is preferably separated and processed further as an aqueous phase.

10 The invention also relates to the use of the (metal) salts of alkylphosphonous acids prepared in accordance with the invention as precursors for chemical syntheses.

15 The invention also relates to the use of the (metal) salts of alkylphosphonous acids prepared in accordance with the invention for the preparation of organo-phosphorus compounds.

20 The invention also relates to the use of the (metal) salts of alkylphosphonous acids prepared in accordance with the invention as flame retardants or for the preparation of flame retardants.

25 The invention relates in particular to the use of the (metal) salts of alkylphosphonous acids prepared in

accordance with the invention for the preparation of flame retardants for thermoplastic polymers, such as polyethylene terephthalate, polybutylene terephthalate or polyamide.

5

The invention relates in particular to the use of the (metal) salts of alkylphosphonous acids prepared in accordance with the invention for the preparation of flame retardants for thermosetting resins, such as
10 unsaturated polyester resins, epoxy resins, polyurethanes or acrylates.

Surprisingly, it has been found that elemental yellow phosphorus can be reacted with alkylating agents in a
15 two-phase system (organic solvent/base) and, if desired, in the presence of a (phase-transfer) catalyst under extremely mild conditions by the process according to the invention to give the (metal) salts of the corresponding alkylphosphonous acid $RP(:O)HOH$.

20

In addition, small amounts of dialkylphosphinic acids, trialkylphosphine oxide $R_3P(:O)$, dialkylphosphine oxide and unidentified phosphorus compounds may be formed; these can be removed from the product mixture in the
25 usual manner. A further byproduct formed is hydrogen, which can easily be separated off from the reaction

mixture. The abovementioned dialkylphosphinic acids can be separated off from the reaction mixture and employed or further processed elsewhere.

5 Surprisingly, the process according to the invention gives neither phosphine (PH_3) nor alkylphosphines (RPH_2 , R_2PH) in significant amounts. Through the choice of suitable reaction conditions - such as the addition of small amounts of alcohols to the organic phase - the
10 formation of all unidentified phosphorus-containing byproducts can be minimized to a surprisingly low content of a few mol% of the yellow phosphorus employed, in favor of the main product, the (metal) salts of alkylphosphonous acid.

15

The process according to the invention can be carried out, for example, by introducing the solvent together with the phase-transfer catalyst and warming the mixture to above the melting point of the yellow
20 phosphorus, then adding the elemental (yellow) phosphorus, cooling the mixture to temperatures of, for example, from -10 to $+30^\circ\text{C}$ with vigorous stirring, and subsequently adding the alkylating agent.

25 The reaction is initiated by addition of the base. When the reaction is complete, the reaction mixture can be

diluted, for example with water, and the readily volatile components (H_2 , PH_3 , RPH_2 , R_2PH and excess alkylating agent, etc.) are subsequently removed.

- 5 This process gives a base-containing/organic two-phase system whose phases are separated. The contents from the phases are determined analytically.

The base-containing phase can be worked up by the known
10 methods of the prior art in order to obtain the pure acids, such as, for example, alkylphosphonous acid (for example by ion exchange or distillation).

The reactants can also be combined in a different
15 sequence, for example by introducing them continuously into a reactor (pressure tube, pressure reactor or cascade) in the above-defined molar ratio and removing them from the reactor again after a residence time of from 0.5 to 2 hours. The organic phase obtained after
20 the phase separation, which still contains the majority of any phase-transfer catalyst employed, is advantageously recycled.

Example 1: Methylphosphonous acid

A solution of 52.2 g (0.1 mol) of tributylhexadecylphosphonium bromide in 1000 ml of toluene was introduced into a 5 l stainless-steel pressure reactor and pre-heated to 60°C. 62 g (2 mol) of yellow phosphorus were added, the mixture was cooled to -10°C with vigorous stirring, and 252 g (2 mol) of dimethyl sulfate were then metered in. The mixture was then warmed to 20°C, and 500 g of 40% aqueous sodium hydroxide solution were metered in over the course of 4 hours, during which the temperature was held at 20°C. Over the course of a further hour, 300 g of water were added, the mixture was then stirred for a further hour, and the reactor was subsequently decompressed via combustion. Two homogeneous liquid phases were obtained, which were separated and analyzed.

The aqueous phase (weight: 930 g) contained 54.6 mol% of methylphosphonous acid, 17.9 mol% of phosphorous acid, 19.7 mol% of hypophosphorous acid, 2.8 mol% of dimethylphosphinic acid in the form of their sodium salts and 3 mol% of dimethyldiphosphine.

The acids can be obtained from the salts prepared in Example 1 in a known manner, for example by ion exchange.

Patent claims

1. A process for the preparation of (metal) salts of alkylphosphonous acids, which comprises reacting
5 elemental yellow phosphorus with halogen-free alkylating agents in the presence of at least one base.
2. A process as claimed in claim 1, wherein the
10 reaction is carried out in a two-phase system comprising at least one base and an organic solvent.
3. A process as claimed in claim 1 or 2, wherein the
15 alkylating agents are dialkyl sulfates, trialkyl phosphates, dialkyl carbonates and/or formic acid ortho-esters.
4. A process as claimed in one or more of claims 1 to
20 3, wherein the organic solvents employed are straight-chain or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible or only partially water-miscible alcohols or ethers, alone or in combination with one another.

5. A process as claimed in one or more of claims 1 to 4, wherein the organic solvent employed is toluene, alone or in combination with alcohols.
- 5 6. A process as claimed in one or more of claims 1 to 5, wherein the bases are hydroxides, carbonates, bicarbonates, amides, alkoxides and/or amine bases.
- 10 7. A process as claimed in one or more of claims 1 to 6, wherein the reaction is carried out in the presence of a phase-transfer catalyst.
- 15 8. A process as claimed in claim 7, wherein the phase-transfer catalyst is a tetraalkylphosphonium halide, triphenylalkylphosphonium halide or tetraorganylammonium halide.
- 20 9. A process as claimed in one or more of claims 1 to 8, wherein the temperature during the reaction is from -20 to +60°C.
10. A process as claimed in one or more of claims 1 to 9, wherein the temperature is from 0 to 30°C.

11. A process as claimed in one or more of claims 1 to 10, wherein the reaction is carried out at a pressure of from 0 to 10 bar.
- 5 12. A process as claimed in one or more of claims 1 to 11, wherein the yellow phosphorus is suspended or dissolved in a solvent or solvent mixture and then reacted with a halogen-free alkylating agent and at least one base.
- 10 13. A process as claimed in one or more of claims 1 to 12, wherein the yellow phosphorus and the halogen-free alkylating agent are reacted in a molar ratio of from 1:1 to 1:3, where the molar ratio of
- 15 yellow phosphorus to base is from 1:1 to 1:5.
14. A process as claimed in one or more of claims 1 to 13, wherein the two-phase system obtained after the reaction is separated and further processed.
- 20 15. The use of a (metal) salt of an alkylphosphonous acid prepared by a process as claimed in claims 1 to 14 as a precursor for chemical syntheses.
- 25 16. The use of a (metal) salt of an alkylphosphonous acid prepared by a process as claimed in claims 1

to 14 for the preparation of organophosphorus compounds.

17. The use of a (metal) salt of an alkylphosphonous
5 acid prepared by a process as claimed in claims 1
to 14 as a flame retardant or for the preparation
of flame retardants.

18. The use of a (metal) salt of an alkylphosphonous
10 acid prepared by a process as claimed in claims 1
to 14 for the preparation of flame retardants for
thermoplastic polymers, such as polyethylene
terephthalate, polybutylene terephthalate or
polyamide.

15
19. The use of a (metal) salt of an alkylphosphonous
acid prepared by a process as claimed in claims 1
to 14 for the preparation of flame retardants for
thermosetting resins, such as unsaturated poly-
20 ester resins, epoxy resins, polyurethanes or
acrylates.

Process for the preparation of (metal) salts of
alkylphosphonous acids I

Abstract

The invention relates to a process for the preparation of (metal) salts of alkylphosphonous acids, which comprises reacting elemental yellow phosphorus with halogen-free alkylating agents in the presence of at least one base.

The invention also relates to the use of the (metal) salts of alkylphosphonous acids prepared by this process.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS FOR PREPARING (METAL) ALKYLPHOSPHONITES I

the specification of which

☒ [X] is attached hereto

☐ [] was filed on _____, 19 ____ as application Serial No. /

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Applications(s) for which Priority is Claimed:

Federal Republic of Germany, 199 23 830.8 of May 25, 1999

And I hereby appoint

Miles B. Dearth, Reg. No. 35,115; Scott E. Hanf, Reg. No. 38,906; Susan Jackson, Reg. No. 41,302; Hesna J. Pfeiffer, Reg. 22,640

all of CLARIANT CORPORATION, address as indicated below, respectively and individually, as my attorneys and/or agents, with full power of substitution, to prosecute this application, and transact all business in the Patent and Trademark Office connected therewith.

Please address all communications to Clariant Corporation, 4331 Chesapeake Drive, Charlotte, North Carolina 28216, whose Facsimile number is 704/395-6727.

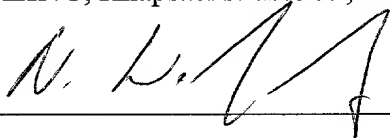
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed: at Hürth, Federal Republic of Germany, this 2nd day of May, 2000

INVENTOR(S) / Residence

1) Dr. Norbert WEFERLING, Knapsackstrasse 39, D-50354 Hürth, Germany

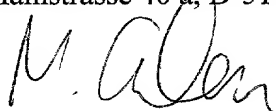
Signature:



Date: May 2, 2000

2) Dr. Martin SICKEN, Mainstrasse 40 a, D-51149 Köln, Germany

Signature:



Date: May 2, 2000

Signature:

Date:

Signature:

Date:

Citizenship: 1) + 2) German

Post Office Address of all Inventors: Clariant GmbH
Werk Knapsack
Patents, Trademarks, Licenses
D-50351 Hürth-Knapsack
Germany